SOIL VAPOR SAMPLING ANALYTICAL SOLUTION FOR USE IN CHARACTERIZING INDOOR AIR RISK

I. INTRODUCTION MAY 2001

Soil vapor sampling, applied for purposes of qualifying and/or quantifying indoor air risk, is today more exacting than it has been historically, when it was used to support source removal and SVE system design. The reasons indoor air poses a greater challenge to soil vapor sampling includes: (1) indoor air risk is often driven by very low volatile organic compound (VOC) concentrations (*e.g.*, concentrations generated by low-level dissolved-phase sources); (2) target indoor air VOC concentrations are often at or below state-of-the-art laboratory analytical detection limits and (3) given such low concentrations, non-steady-state effects (particularly at or near the surface boundary) are likely to influence/bias soil vapor sampling.

In efforts to render soil vapor sampling more exacting yet unburdened by a level of technical complexity which often characterizes environmental modeling, an easy to use and understand steady-state analytical solution has recently been derived to assist project managers in both the public and private sectors. This mathematical relationship provides information regarding two fundamentally important considerations with respect to sampling soil vapor for purposes of characterizing indoor air risk:

- the equation estimates a minimum sampling depth necessary to detect target VOCs, and
- the equation provides information that can be used to identify sampling techniques most appropriate for use at a given site.

The equation therefore answers the following questions:

- how do we know that we are likely to detect VOCs at a given sampling depth?
- how do we know what sampling and analytical technique is appropriate?

II. PURPOSE

The purpose of this document is to:

- provide the equation,
- illustrate its application to a representative set of environmental parameters, and
- provide questions and answers to help guide its application.

1. The Equation

The equation is an analytical solution to a steady-state differential equation which answers the following question: if the concentration of a VOC in groundwater, C_w , is known, and the depth to the water table, d, is known, then at what minimum depth below surface, z, must one sample to assure that the vapor phase VOC concentration meets or exceeds a pre-specified target concentration? Typically, this target concentration is set by the user to the analytical detection limit (e.g., method detection limit (MDL), lower limit of detection (LLD), practical quantitation limit (PQL) or reporting limit (RL)).

The non-steady-state partial differential equation is:

$$\partial C_{sv}/\partial t = -v \partial C_{sv}/\partial z + D_{eff} \partial^2 C_{sv}/\partial z^2$$
 (1)

where,

 C_{sv} is the concentration of a volatile organic compound (VOC) in soil vapor D_{eff} is the effective diffusion coefficient in soil v is the pore velocity z is the space coordinate in the direction of diffusion

Under steady-state conditions, the time-dependent term, $\partial C_{sv}/\partial t$, is zero, and the equation simplifies to an ordinary differential equation. In addition, we assume that the transport of contaminant in the soil vapor is by diffusion, and that the advective transport (flow) is negligible. These assumptions result in the following second order ordinary differential equation:

$$0 = D_{\text{eff}} \partial^2 C_{\text{sv}} / \partial z^2$$

Note that by dividing both sides of the equation by the effective diffusion coefficient eliminates this parameter, which is therefore absent from the steady state equation. This feature of the steady-state equation therefore reduces the number of parameters needed to use the equation.

The solution to this differential equation is subject to the following assumptions and boundary conditions: 1) the soil vapor concentration at the groundwater interface (z = d) is in equilibrium with the groundwater per Henry's Law; and 2) the soil vapor concentration at the ground surface (z = 0) is zero. Note that z is defined only from 0 < z < d; the implications of this will be discussed later. The solution may be most conveniently expressed in the following algebraic form:

$$z/d = C_{sv} / (K_h C_w) * RT$$
 (2)

where,

z is the target sampling depth (feet below grade (ft BG))

d is the depth to groundwater (ft BG)

C_{sv} is the concentration of a volatile organic compound (VOC) in soil vapor (ug/l)

C_w is the concentration of a VOC in groundwater (ug/l)

K_b is the Henry's constant (atm m³/mol)

R is the Ideal Gas Law Constant (8.206E-05 atm m3/mole K)

T estimated absolute soil temperature (~283°K)

2. Applying the Equation

The following example illustrates how the equation is applied; these calculations, though straightforward, are provided for the project manager who has limited time to research how the equation may be best applied. Important: application of this equation is best understood if the following example is understood in context with the Questions & Answers provided in Section III.

Example: At a hypothetical site, a low-level dissolved-phase plume containing trichloroethylene (TCE) and perchloroethylene (PCE) is migrating underneath a residential area. Because the plume is migrating from a Superfund site where investigation has occurred, the site conceptual model (*e.g.*, geology, hydrology and the levels of VOCs) is generally well understood. However, there is a concern that TCE and the 'daughter products,' vinyl chloride (VC) and 1,1-dichloroethylene (1,1-DCE), may be present in soil vapor underneath the residential area at concentrations that may pose an indoor air risk. Limited direct sampling of indoor air has been conducted using Summa® canisters. However, for a variety of reasons, this data does not appear to provide a requisite basis for decision making (*e.g.*, a number of residential home owners have refused to allow indoor air sampling; even for those homes where direct sampling has been conducted, the results suggest the data suffers from indoor source bias and/or severe spatial and temporal transience). It would be helpful to know whether soil vapor sampling may help to qualify/quantify indoor air risk at the site.

a. Input Parameters

The following parameters are known (or can be reasonably estimated):

- depth to groundwater in the area of the residential homes is generally around 10 ft BG;
- the concentrations of 1,1-DCE and TCE in the groundwater are approximately 1.0 and 100 ug/l, respectively; the available data suggests vinyl chloride may range from 0.1 to 1 ug/l; and
- although the method detection limit (MDL) of the laboratory method (*e.g.*, TO14) is quite low (~ 0.02 ug/l), there is concern the practical quantitation limit (PQL) will be higher (~ 4 ug/l).

The input parameters are therefore:

 $\begin{array}{lll} C_{sv} & 4 \text{ ug/l} \\ d & 10 \text{ ft BG} \\ K_h \text{ (VC)} & 0.695 \text{ atm m}^3 \text{ /mol} \\ K_h \text{ (1,1-DCE)} & 0.154 \text{ atm m}^3 \text{ /mol} \\ K_h \text{ (TCE)} & 0.009 \text{ atm m}^3 \text{ /mol} \\ R & 8.206\text{E-}05 \text{ atm m}^3 \text{/mole K} \\ T & 283 ^{\circ} \text{K} \end{array}$

b. Calculate

The ratio, z/d, in equation (2) expresses the sampling depth as a fraction of the depth to groundwater that is required to intercept a soil vapor concentration equal to the specified C_{sv} . Equation (2) can be solved directly for a single z/d value corresponding to one C_w concentration; however, additional insight can be gained by plotting z/d for several values of C_w using a spreadsheet application. Selected values are tabulated below. (Note: z/d cannot be greater than 1 because z is defined over the range 0 < z < d):

x-axis	y-axis (1)	y-axis (2)	y-axis (3)
Cw (ug/l)	z/d (VC)	z/d (1,1-DCE)	z/d (TCE)
0.01	1.00	1.00	1.00
0.05	1.00	1.00	1.00
0.1	1.00	1.00	1.00
0.5	0.33	1.00	1.00
1	0.16	0.74	1.00
5	0.03	0.15	1.00
10	0.02	0.07	1.00
20	0.01	0.04	0.63
30	0.01	0.02	0.42
40	0.00	0.02	0.32
50	0.00	0.00	0.25
100	0.00	0.01	0.13

c. Plot

The plot of z